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**TRANSMITTAL LETTER TO THE UNITED STATES
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CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/049604

INTERNATIONAL APPLICATION NO.

PCT/GB00/03184

INTERNATIONAL FILING DATE

August 16, 2000

PRIORITY DATE CLAIMED

August 17, 1999

TITLE OF INVENTION

MELT-PROCESSABLE THERMOPLASTIC COMPOSITIONS

APPLICANT(S) FOR DO/EO/US

Paul EUSTACE, Nicholas John MARSTON, John Robert OLIVER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau. (attach form IB 308)
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☐ Other items or information:
- 20a. ☐ **For purposes of examination, please insert the annexes to the IPER, so that the application will comprise the following pages of the English translation:**

Specification: Original pages	Amended pages
Claims: Original claims	Amended claims

JC12 Rec'd FCT/FTO 14 FEB 2002

Figure 1 consists of 12 micrographs arranged vertically, labeled 1 through 12. Each micrograph shows a different stage of chick embryo development.

- Micrograph 1: A single cell (zygote) with a prominent nucleus.
- Micrograph 2: Two cells (2-cell stage).
- Micrograph 3: Four cells (4-cell stage).
- Micrograph 4: Eight cells (8-cell stage).
- Micrograph 5: A morula, a solid ball of cells.
- Micrograph 6: A blastula, showing a hollow sphere of cells with a central cavity.
- Micrograph 7: A gastrula, showing the beginning of tissue differentiation.
- Micrograph 8: A stage showing the formation of the neural tube.
- Micrograph 9: A stage showing the development of the somites.
- Micrograph 10: A stage showing the development of the heart and other internal organs.
- Micrograph 11: A stage showing the development of the head and neck.
- Micrograph 12: A fully developed chick embryo, ready to hatch from the egg.

 The labels 1 through 12 are positioned to the left of each corresponding micrograph.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Paul EUSTACE et al.

Int'l. Appl. No.: PCT/GB00/03184

Int'l Filing Date: August 16, 2000

For: MELT-PROCESSABLE
THERMOPLASTIC
COMPOSITIONS

Art Unit: NOT YET ASSIGNED

Examiner: NOT YET ASSIGNED

Atty. Docket No.: 31229-178457

Customer No.



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PATENT TRADEMARK OFFICE

Preliminary Amendment

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to calculation of the fees, please amend claims 3, 6-10, 13-15, 18-22, 25, and 26 attached to the specification and add claims 27-30 as follows:

3. (Amended) A composition according to Claim 1, wherein said particulate polymer is formed from the residues of a monomer mixture comprising at least 50 wt% methyl methacrylate.

6. (Amended) A composition according to Claim 1, wherein said monomer mixture includes at least 0.1 wt% of a comonomer which is capable of forming cross-linking with the polymer.

7. (Amended) A composition according to Claim 1, wherein said particulate polymer is formed from the residues of a monomer mixture comprising 70 - 95 wt% MMA, 5 - 30 wt% of a copolymerisable acrylic comonomer and 0.1 - 5 wt% of a comonomer which is capable of forming cross-linking within the polymer.

8. (Amended) A composition according to Claim 1 which includes at least 1 wt% and less than 40 wt% of said particulate polymer.

9. (Amended) A composition according to Claim 1, wherein the particles of said particulate polymer are of a size such that they could pass through a 500 μm sieve.

10. (Amended) A composition according to Claim 1, wherein at least 20 wt% of particles of said particulate polymer are between 60 (250 μm) and 80 (177 μm) mesh.

13. (Amended) A method according to Claim 11, wherein said melt-processable polymer and said particulate polymer are mixed by extrusion under conditions such that particles of said particulate polymer are broken down.

14. (Amended) A method according to Claim 11, wherein said melt-processable polymer and said particulate polymer are not caused to chemically react during said mixing and/or extrusion.

15. (Amended) A method of forming an article which comprises shaping a melt-processable thermoplastic composition according to Claim 1 in order to form said article.

18. (Amended) A method according to Claim 15, wherein said composition is extruded or co-extruded.

19. (Amended) A method according to Claim 15, wherein said article includes a substrate and a capstock material wherein said capstock material comprises said melt-processable thermoplastic composition.

20. (Amended) A method according to Claim 15, wherein said article is a building component.

21. (Amended) A method according to Claim 15, wherein said article is a component for use in construction and is a co-extruded component comprising a substrate made of PVC, HIPS or ABS and said melt-processable thermoplastic material provided as a capstock thereon.

22. (Amended) A method according to Claim 15, wherein when a surface of the article formed of said thermoplastic composition is tested for impact resistance in accordance with ASTM D4226, the mean failure height is not less than 7.5 inches (19.05 cm).

25. (Amended) An article which includes a substrate and a capstock material prepared from a thermoplastic composition as described in Claim 1.

26. (Amended) An article according to Claim 19 wherein said capstock layer or material has a thickness of less than 200 μm .

27. (New) A method of forming an article which comprises shaping a melt-processable thermoplastic composition according to Claim 11 in order to form said article.

28. (New) An article which includes a substrate and a capstock material prepared from a thermoplastic composition as described in Claim 11.

29. (New) An article which includes a substrate and a capstock material prepared from a thermoplastic composition as described in Claim 24.

30. (New) An article according to Claim 24 wherein said capstock layer or material has a thickness of less than 200 μm .

REMARKS

This Preliminary Amendment is made to eliminate multiple claim dependency. Examination on the merits of the application is requested. A marked up version showing the changes made to the claims is attached.

Respectfully submitted,

Date: FEBRUARY 14, 2002



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VERSION WITH MARKINGS TO SHOW CHANGES MADE

3. (Amended) A composition according to Claim [or Claim 2] 1, wherein said particulate polymer is formed from the residues of a monomer mixture comprising at least 50 wt% methyl methacrylate.

6. (Amended) A composition according to Claim 1 [any preceding claim], wherein said monomer mixture includes at least 0.1 wt% of a comonomer which is capable of forming cross-linking with the polymer.

7. (Amended) A composition according to [any preceding claim] Claim 1, wherein said particulate polymer is formed from the residues of a monomer mixture comprising 70 - 95 wt% MMA, 5 - 30 wt% of a copolymerisable acrylic comonomer and 0.1 - 5 wt% of a comonomer which is capable of forming cross-linking within the polymer.

8. (Amended) A composition according to [any preceding claim] Claim 1 which includes at least 1 wt% and less than 40 wt% of said particulate polymer.

9. (Amended) A composition according to [any preceding claim] Claim 1, wherein the particles of said particulate polymer are of a size such that they could pass through a 500 μ m sieve.

10. (Amended) A composition according to [any preceding claim] Claim 1, wherein at least 20 wt% of particles of said particulate polymer are between 60 (250 μm) and 80 (177 μm) mesh.

13. (Amended) A method according to Claim 11 [or Claim 12], wherein said melt-processable polymer and said particulate polymer are mixed by extrusion under conditions such that particles of said particulate polymer are broken down.

14. A method according to [any of Claims 11 to 13] Claim 11, wherein said melt-processable polymer and said particulate polymer are not caused to chemically react during said mixing and/or extrusion.

15. (Amended) A method of forming an article which comprises shaping a melt-processable thermoplastic composition according to [any of Claims 1 to 10 or as prepared according to any of Claims 11 to 14] Claim 1 in order to form said article.

18. (Amended) A method according to [any of Claims 15 to 17] Claim 15, wherein said composition is extruded or co-extruded.

19. (Amended) A method according to [any of Claims 15 to 18] Claim 15, wherein said article includes a substrate and a capstock material wherein said capstock material comprises said melt-processable thermoplastic composition.

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20. (Amended) A method according to [any of Claims 15 to 19] Claim 15, wherein said article is a building component.

21. (Amended) A method according to [any of Claims 15 to 20] Claim 15, wherein said article is a component for use in construction and is a co-extruded component comprising a substrate made of PVC, HIPS or ABS and said melt-processable thermoplastic material provided as a capstock thereon.

22. (Amended) A method according to [any of Claims 15 to 21] Claim 15, wherein when a surface of the article formed of said thermoplastic composition is tested for impact resistance in accordance with ASTM D4226, the mean failure height is not less than 7.5 inches (19.05 cm).

25. (Amended) An article which includes a substrate and a capstock material prepared from a thermoplastic composition as described in [any of Claims 1 to 10 or when prepared in a method according to any of Claims 11 to 22 or 24] Claim 1.

26. (Amended) An article according to [any of Claims 19, 21, 24 or 25] Claim 19, wherein said capstock layer or material has a thickness of less than 200 μm .

Melt-Processable Thermoplastic Compositions

The present invention relates to melt-processable thermoplastic compositions, especially to acrylic compositions. Particularly, although not exclusively, the invention relates to compositions for making articles having surfaces exhibiting relatively low gloss.

Thermoplastic compositions, especially acrylic compositions, are used in a variety of applications, some of which may demand a particular surface appearance, such as low gloss. Acrylic compositions containing gloss modifiers, usually to reduce the surface gloss of the compositions, are already known and used in the industry. Commonly used gloss modifying compounds are talcs or other inorganic compounds. Talcs can generally be used to reduce surface gloss to a minimum of about 20 (measured at 75° observation angle). However, when a very low gloss or matte surface finish is required, e.g. for building components such as vinyl siding or the like, talcs or other conventional gloss reducing compounds may be ineffective or may be required to be present at such high levels that the other properties of the composition are compromised. There is therefore a need for an acrylic composition which is suitable for producing articles which have a relatively low gloss surface but which are comparable in physical properties to higher gloss acrylic compositions.

WO-A-97/14749 describes acrylic compositions having the appearance of a natural granite comprising a polymethyl methacrylate matrix having dispersed within it particles comprising 75-90wt% of PMMA, at least 10% of an

ethylenically unsaturated comonomer and at least 0.4 wt% of a cross-linker. The granite articles are prepared by casting a syrup of polymer in monomer containing the particles and curing to produce a glossy article.

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US-A-5242968 describes a cast acrylic article having a textured but glossy surface formed by casting a polymer in monomer syrup containing ground PMMA particles in a cell and curing the mixture so that it polymerises.

10

US-A-5304592 describes acrylic articles which contain particles of a thermoplastic and/or thermoset plastic which are visually different from the acrylic matrix in which they are suspended and which have different viscosities or melting points from the plastic of the matrix yet which have a similar density to the matrix so that the particles do not settle during processing.

It is an object of the present invention to provide a melt-processable thermoplastic composition which address problems associated with prior art compositions.

According to a first aspect of the present invention, there is provided a melt-processable thermoplastic composition comprising;

- a) 50-99.5 wt% of a melt-processable thermoplastic polymer; and
- b) 0.5-50 %wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt% of methyl methacrylate (MMA), at least 0 - 50 wt% of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10

wt% of a copolymerisable cross-linking monomer, said particles having a maximum dimension of 5 mm.

The thermoplastic polymer preferably forms a matrix throughout which the particulate polymer is dispersed. The particulate polymer may, however, be more or less concentrated in some parts of the matrix than others as a result of a melt-processing method which may be used to form the composition. Nevertheless, it has been found that the incorporation of the particulate polymer into the melt-processable thermoplastic polymer matrix enables articles to be produced by melt-processing techniques such as injection moulding or extrusion, which have an excellent low-gloss surface finish.

The melt-processable thermoplastic polymer may be selected from a range of materials, e.g. FVC, polystyrene, polyesters, styrene-acrylonitrile copolymers and terpolymers, e.g. ABS, styrene-acrylonitrile (SAN), acrylonitrile-styrene-acrylic (SAN), polycarbonate, nylon, acrylic polymers such as polymethylmethacrylate and its copolymers with other (meth)acrylates, provided that the polymer(s) selected may be melt processed at a temperature which is below the temperature at which the particulate acrylic polymer thermally degrades, e.g. below about 300°C. The melt-processable polymer may also comprise a blend of thermoplastic polymers. In one preferred form of the invention, the melt-processable thermoplastic polymer which forms a matrix is a polymethylmethacrylate (PMMA) homopolymer or copolymer derived from a monomer mixture comprising 60 - 100 wt% methyl methacrylate and 0 - 40 wt% of at least one other copolymerisable alkyl acrylate or methacrylate. A preferred PMMA matrix is a copolymer of

60 - 98 wt% methyl methacrylate and 2 - 40 wt% of at least one other copolymerisable alkyl acrylate selected from a C₁₋₄alkyl, e.g. methyl, ethyl or butyl, hydroxyethyl, 2-ethylhexyl, cyclohexyl or phenyl acrylates. Of the
5 aforesaid, a C₁₋₄ alkylacrylate (especially n-alkyl acrylates where isomers can exist) is preferred; methyl, ethyl and butyl acrylates are more preferred; ethyl and butyl (especially n-butyl) acrylates are especially preferred; and ethyl acrylate is most preferred. A
10 preferred copolymer comprises 80 - 98 wt% methyl methacrylate residues and 2 - 20 wt% of the residues of at least one said alkyl acrylate. Preferably, said preferred copolymer comprises at least 82 wt%, more preferably at least 84 wt%, especially at least 85 wt% methyl
15 methacrylate. The amount of methyl methacrylate may be less than 95 wt%, suitably less than 92 wt%, preferably less than 90 wt%, more preferably less than 88 wt%, especially for use in construction, such as for vinyl sidings as hereinafter described. Said preferred copolymer
20 may include at least 5 wt%, preferably at least 8 wt%, more preferably at least 10 wt%, especially at least 12 wt% of said at least one said alkyl acrylate. Preferably said at least one alkyl acrylate comprises a single alkyl acrylate. The matrix polymer may additionally contain
25 residues of other materials, e.g. thermal stabilisers (e.g. alkyl mercaptans as are commonly used in moulding polymer formulations), polymerisation initiators, lubricants, mould release agents, UV and light stabilisers, pigments, dyes, opacifiers, impact modifying
30 compounds (including rubbery materials and core-shell type impact modifying particles) and flame retardants. Preferably, the matrix polymer includes a major amount of melt-processable thermoplastic polymer, especially a major

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amount of said polymethylmethacrylate homopolymer or copolymer.

In the context of this specification, a "major" amount
s suitably refers to at least 60 wt%, preferably at least 75
wt%, more preferably at least 90 wt%, especially at least
95 wt%.

The melt flow index (MFI) of said melt-processable
10 thermoplastic polymer at 230°C using a 3.8 Kg weight over
10 minutes (according to DINS3735) is suitably at least 5.
For some, preferred applications, said MFI may be at least
10, suitably at least 15, preferably at least 20, more
preferably at least 25 and in some cases at least 27. The
15* MFI may be less than 35, preferably less than 32.

The particulate polymer is a homopolymer or copolymer
which comprises 50 - 100 wt% MMA, at least 0 - 50 wt% of
an ethylenically unsaturated comonomer comprising at least
20 one alkyl acrylate or methacrylate and 0 - 10 wt% of a
copolymerisable cross-linking monomer. Suitable particles
are described in WO-A-97/14749 for incorporation into cast
acrylic products to impart the appearance of granite.

25 Said particulate polymer is suitably formed from the
residues of a monomer mixture comprising at least 50 wt%,
preferably at least 59.9 wt%, more preferably at least
69.9wt%, especially at least 79.9 wt% of methyl
methacrylate (MMA) In some cases, the amount of said MMA
30 may be at least 82 wt% or even 83 wt%. The amount of MMA
may be less than 99 wt%, suitably less than 95 wt%,
preferably less than 90 wt%, more preferably less than 88
wt%, especially less than 86 wt%. Said monomer mixture

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may also include at least 1 wt%, suitably at least 5 wt%, preferably at least 10 wt%, more preferably at least 12 wt%, especially at least 14 wt% of a copolymerisable acrylic comonomer. The amount of said copolymerisable acrylic comonomer may be less than 50 wt%, suitably less than 30 wt%, preferably less than 25 wt%, more preferably less than 20 wt%, especially less than 18 wt%. Said acrylic comonomer may be of a type as described above for said copolymerisable alkyl acrylate of said PMMA matrix.

10 Said comonomer is preferably an alkyl acrylate, especially a C₁₋₄ alkyl acrylate, preferred examples of which include ethyl acrylate and butyl acrylate. The particulate polymer may be formed from one or more copolymerisable acrylic comonomers. Where more than one acrylic copolymer

15⁴ is used in conjunction with MMA described, suitably the sum of the wt% of the copolymerisable acrylic comonomers (excluding multi-functional acrylic monomers) is as described above. Said monomer mixture may also include at least 0.1 wt%, suitably at least 0.2 wt%, preferably at

20 least 0.3 wt%, more preferably at least 0.4 wt% of a comonomer which is capable of forming cross-linking with the polymer. The amount of said comonomer may be less than 10 wt%, suitably less than 5 wt%, preferably less than 4 wt%, more preferably less than 3 wt%, especially

25 less than 2 wt%. In some cases, 1 wt% or less (preferably less than 1 wt%) of said comonomer may be used. Preferred comonomers capable of forming cross-linking are multi-functional and are preferably multi-functional acrylate monomers, for example di(alk)acrylate compounds such as

30 dimethacrylate compounds.

In one case, said particulate polymer is formed from the residues of a monomer mixture comprising 70 - 95 wt% MMA,

5 - 30 wt% of a copolymerisable acrylic comonomer (preferably an alkyl acrylate) and 0.1 - 5 wt% of a comonomer which is capable of forming cross-linking within the polymer.

5

Said thermoplastic composition may include at least 1 wt%, preferably at least 3 wt%, more preferably at least 5 wt%, especially at least 6 wt% of said particulate polymer. The amount of said particulate polymer may be 40 wt% or less, preferably 30 wt% or less, more preferably 20 wt% or less, especially 15 wt% or less.

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The particulate polymer may have a wide size distribution and particles thereof may have a maximum size of about 15 5mm. Preferably, the particles have a maximum dimension which is less than 1mm, for example particles which pass through a 500 μm sieve may be used. Preferably, a major amount, more preferably all, of said particles of said particulate polymer of a type described in (b) above can pass through a 350 μm sieve, more preferably through a 300 μm sieve, especially through a 250 μm sieve. In one preferred form particles having a size distribution from <10 to about 600 μm are used. The weight averaged diameter of said particles of said particulate polymer may be 25 greater than 100 μm , suitably greater than 150 μm . The weight averaged diameter may be less than 500 μm , suitably less than 400 μm , preferably less than 300 μm , more preferably less than 250 μm . The aforementioned weight averaged diameters may be assessed as described in ASTM 30 D1921.

Suitably, at least 20%, preferably at least 40%, more preferably at least 60%, especially at least 80% of

particles of said particulate polymer are between 60 (250 μ m) and 80 (177 μ m) mesh.

It has been found that in high shear processes such as
5 extrusion and injection moulding, the particles of said
particulate polymer are broken up into smaller particles
so that, surprisingly, the particles do not produce an
unduly rough or lumpy surface, even when particles as
large as 250 μ m are used in the thermoplastic composition
10 and the composition is extruded to form a layer having a
thickness below 100 μ m. The particle size to be used in
any situation may be selected based upon its availability
and the constraints of handling and processing such
particles. However, preferred particle sizes are as
15 described.

The particulate polymer is preferably made by grinding a
larger piece or pieces of polymer of the required
composition. It has been found that the particles formed
20 in this way are irregular with many corners and sharp
edges. The polymer may be made by a variety of
polymerisation methods, e.g. suspension, solution,
emulsion, or bulk polymerisation methods.

25 It has been found that when a sheet of the thermoplastic
polymer composition has been extruded and calendered,
there are marked differences between the gloss on the
surface of the sheet which has been in contact with the
calender rolls and the opposite surface which has been in
30 contact with air. For this reason, when the low-gloss
thermoplastic composition of the invention is applied over
a layer of a different polymer, e.g. by coextrusion, it is
preferred that the surface of the low-gloss composition is

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processed so that it is run through the calender roll stack on the air side of the sample.

According to a second aspect of the present invention, there is provided a method of preparing a melt-processable thermoplastic composition, (preferably according to said first aspect), the method comprising contacting, preferably mixing:

- 10 a) 50-99.5 wt% of a melt-processable thermoplastic polymer; and
 - b) 0.5-50 %wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt% of methyl methacrylate (MMA), at least 0 - 50 wt% of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt% of a copolymerisable cross-linking monomer, said particles having a maximum dimension of 5 mm.
- 20 Said particulate polymer may have a hardness of less than 90 when measured on the Rockwell Hardness M-Scale according to ISO2039-2.

Said melt-processable polymer and said particulate polymer are preferably not cast. Said melt-processable polymer and said particulate polymer are preferably mixed by extrusion, suitably using a high shear extruder. Said melt-processable polymer and said particulate polymer may be subject to a shear rate of at least $100s^{-1}$, preferably at least $115s^{-1}$, more preferably at least $130s^{-1}$, especially at least $140s^{-1}$ during said mixing. The shear rate may be less than $200s^{-1}$, preferably less than $180s^{-1}$, more preferably less than $160s^{-1}$.

Said mixing by extrusion is preferably undertaken under conditions such that particles of said particulate polymer are broken down. Thus, preferably, the weight averaged diameter of said particulate polymer before said extrusion
5 is greater than after said extrusion.

Said mixed/extruded melt-processable polymer and said particulate polymer is preferably formed into discrete units, for example pellets, of said melt-processable
10 thermoplastic composition, suitable for subsequent use.

Preferably, said melt-processable polymer and said particulate polymer are not caused to chemically react during said mixing and/or extrusion and, more preferably,
15 are not caused to react at any stage in the preparation of said discrete units. Thus, preferably the melt-processable polymer is not cured during and/or after contact with said particulate polymer. Especially, said melt-processable polymer and said particulate polymer do not chemically
20 react at any stage, for example even up to the formation of an article of a type described herein.

The preparation of said particulate polymer preferably includes the polymerisation of a monomer mixture which
25 suitably includes monomers and/or other ingredients described herein, suitably in the amounts described herein. The polymer formed is preferably subjected to a size reduction step suitably so as to produce particles having particle sizes as described herein. The particles
30 are then suitably mixed with said melt-processable thermoplastic polymer to form said melt-processable thermoplastic composition.

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According to a third aspect of the invention, there is provided a method of forming an article which comprises shaping a melt-processable thermoplastic composition according to said first aspect or prepared according to
5 said second aspect in order to form said article.

In the method, said melt-processable thermoplastic composition may be subjected to conditions such that particles of the particulate polymer in said melt-
10 processable thermoplastic composition are broken down, thereby to reduce their size. Thus, preferably, the weight averaged diameter of said particulate polymer before said shaping is greater than after said shaping. Preferably, the melt-processable thermoplastic composition and/or the
15 conditions to which this is subjected to form the article is/are selected such that a surface of the article formed of said thermoplastic composition includes substantially no particles of diameter of greater than 100 μm . This may be assessed microscopically, for example by incident light
20 optical microscopy and by scanning electron microscopy of sections taken perpendicularly to the surface.

In the method, suitably said melt-processable thermoplastic composition is subjected to a shear rate of
25 at least 100s^{-1} , preferably at least 115s^{-1} , more preferably at least 130s^{-1} , especially at least 140s^{-1} during the shaping of said article. However, where said melt-processable thermoplastic composition is co-extruded, for example with PVC, a low shear extruder may be used in
30 which case the shear rate will be lower than these discussed above.

The composition may be shaped in the form of sheets or film. It may be extruded or moulded into various shapes or co-extruded or laminated onto other materials, for example rigid or foamed forms of ABS, PVC, polystyrene polymers
5 including HIPS and other modified styrene polymers, or polyolefins. The composition may also be co-extruded or laminated onto metals. Sheets prepared as described (e.g. co-extruded or laminated sheets) may be thermoformed or otherwise formed into a desired shape by a suitable means.

10

Advantageously, where injection moulding is used, low surface gloss can be achieved even on highly polished moulds. This may provide a route to producing trim parts to match low gloss extruded or co-extruded panels or to
15 make clear plaques.

The composition may advantageously be used to provide a low gloss, pigmented, co-extruded capstock for less weatherable materials such as PVC (e.g. for vinyl siding,
20 window frames and sheet), HIPS (e.g. for shutters, doors, sheet) and ABS (e.g. for shutters, doors, sheet and window frames).

The method may include preparing a layer from said melt-processable thermoplastic composition which is thinner
25 than the diameters of some particles of particulate polymer used to prepare said melt-processable thermoplastic composition.

30 According to a fourth aspect of the invention, there is provided an article made in a method according to said third aspect.

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Thus, suitably, there is provided an article formed by shaping a molten thermoplastic composition formed by melting an acrylic composition comprising:

- 5 a) 50 - 99 wt% of a melt-processable thermoplastic polymer and
b) 0.5 - 50% wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt% of MMA, at least 0 - 50 wt% of an ethylenically unsaturated
10 comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt% of a copolymerisable cross-linking monomer said particles, having a maximum dimension of 5 mm.

- 15 The article need not be entirely formed from the molten thermoplastic composition. There are many applications in which an article may comprise other materials, e.g. it may be a laminate of the thermoplastic composition and another material or the thermoplastic composition of the invention
20 may form only a surface coating on an article. Such composite articles may be formed by forming a separate thermoplastic layer and bonding it to the finished article or the thermoplastic layer may be applied by techniques such as coextrusion with another thermoplastic or by
25 extrusion coating.

Said article may be a coextruded or laminated component. Said article preferably includes a substrate and a capstock material wherein said capstock material comprises
30 said melt-processable thermoplastic composition.

Said component may be for use in construction.

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Said component may be for use in construction of a building. For example, it could be a solid or coextruded building component, for example a soffit board, barge board, fascia board, cladding board, siding, gutter, pipe, shutters, window casement, window board, window profile, conservatory profile, door panels, door casement, roofing panel, architectural accessory or the like. A preferred component for use in construction is a co-extruded component comprising a substrate, for example made of PVC, HIPS or ABS (especially PVC), and said melt-processable thermoplastic material provided as a capstock thereon. An especially preferred component is vinyl siding comprising PVC and a capstock of said thermoplastic material.

15-⁴ Said component may be for use in constructing a vehicle or in another automotive application, both as a bulk material or as a co-extruded laminate. Such applications include, but are not limited to, decorative exterior trim, cab mouldings, bumpers (fenders), louvers, rear panels, accessories for buses, trucks, vans, campers, farm vehicles and mass transit vehicles, side and quarter panel trim or the like.

Preferably, a surface of the article formed of said thermoplastic composition has a roughness (Ra) of less than 2000 angstroms, preferably less than 1750 angstroms. The roughness may be at least 350 angstroms.

Suitably, a surface of the article formed of said thermoplastic composition has a surface gloss, measured at a 75° observation angle (according to ASTM D3679), of less than 85, preferably less than 75, more preferably less than 65, especially less than 55. In a preferred

embodiment, the surface gloss, measured as described, is in the range 4.5 to 30, more preferably 9 to 20.

Suitably, when a surface of the article formed of said thermoplastic composition is tested for impact resistance in accordance with ASTM D4226, the mean failure height is not less than 7.5 inches (19.1 cm), more preferably not less than 9.5 inches (24.1 cm), especially not less than 10.5 inches (26.7 cm). The mean failure height may be less than 15 inches (38.1 cm).

According to a fifth aspect, there is provided an article which comprises a thermoplastic composition, wherein said article and/or said composition(s) are as described in any statement herein.

According to a sixth aspect of the invention, there is provided an article formed from a thermoplastic composition which comprises a melt-processable thermoplastic polymer and a particulate polymer, wherein the weight averaged diameter of particles of said particulate polymer prior to formation of said article is greater than the diameter after formation of the article.

According to a seventh aspect of the invention, there is provided a method of forming an article which comprises a substrate and, on the substrate, a capstock layer, the method comprising: selecting, for example preparing, a melt-processable thermoplastic composition comprising a melt-processable thermoplastic polymer and a particulate polymer wherein some of the particles of the particulate polymer have a diameter of $x \mu\text{m}$; and extruding, preferably co-extruding, said selected composition to form a capstock

layer of a thickness less than $x \mu\text{m}$. The thickness may be less than 95% of x , preferably less than 75% of x , more preferably less than 50% of x .

- 5 The invention extends to an article which includes a substrate and a capstock material prepared from a thermoplastic composition as described herein.

A capstock layer as described herein may have a thickness
10 of less than $200 \mu\text{m}$, preferably less than $175 \mu\text{m}$, more preferably less than $150 \mu\text{m}$, especially less than $125 \mu\text{m}$. The thickness may be greater than $50 \mu\text{m}$. A thickness of about $100 \mu\text{m}$ is preferred.

- 15 Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

- 20 Specific embodiments of the invention will now be described, by way of example.

Example 1

- 25 A mixture containing a 92% wt commercial acrylic polymer DIAKON[™] MG102 (Ineos Acrylics, U.K.) which is a copolymer of methyl methacrylate and ethyl acrylate and has a molecular weight of approximately 90,000 and 8% of a white pigmented masterbatch was compounded together and pelleted
30 using a Werner & Pfleiderer ZSK30 30mm twin screw extruder running at 230°C and 275 rpm. The resulting pellets were extruded into a 1mm thick x 100 mm wide sheet using a 1.5" (30mm) single screw extruder operating at 230°C and at a

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line speed of approximately 1m/minute. The extruded sheet was run through a 3-roll calendering stage upon exit from the extruder. The rolls were heated to about 80°C and were 50mm in radius.

5

The gloss of each surface of the sheet was measured using a Rhopoint Novo-Gloss meter measuring at an angle of 60°C. As will be understood by those experienced in the art of extruding thermoplastic sheet, one surface is in contact with the heated calendering rolls for longer than the other surface and so these surfaces were measured separately. The surface in contact with the rolls for the longest time is referred to as "highly calendered (hc)" whilst the other surface is referred to as "less calendered (lc)". The gloss of each surface was measured at 10 positions along the direction of extrusion of the sheet and the average result is shown in the Table 1.

15⁴

Preparation of cross-linked acrylic particles

A cross-linked acrylic polymer was made by bulk polymerisation in a sealed nylon bag a monomer mixture comprising 83% MMA, 8% n-butyl acrylate, 8% ethyl acrylate and 1% ethylene glycol dimethacrylate together with initiators and stabilisers.

25

The mixture was subjected to a pre-programmed thermal cycle as conventionally used for bulk polymerisation processes and then cooled. After cooling to ambient temperature, the bag and thermocouple were removed and discarded. The resultant polymer was ground and sieved with a standard wirecloth sieve. The sieve fractions which passed through a standard US 60 mesh sieve (aperture size 250 µm) were used for these Examples. Particle size

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analysis showed that 82% of the particles were between 60 (250 μm) and 80 (177 μm) mesh. The particles appeared to be of irregular shape approximating to pyramidal.

- 5 The particles of cross-linked acrylic polymer were added to the polymer and colour masterbatch mixture. The mixture was compounded using a ZSK 30 extruder (at 230°C, 275 rpm) and a shear rate of about -140s^{-1}) and pelletised and then sheet samples were extruded and their gloss
10 measured, as described above.

Table 1

Particle content (wt%)	Surface	Gloss units
0	hc	87
	lc	87
10	hc	65
	lc	46
20	hc	48
	lc	26

- The results show that the presence of the cross-linked
15 acrylic particles reduced the gloss of both of the surface of the extruded sheet significantly. A difference in gloss between the surfaces of the same sheet was also noted for those samples which contained the particles but not for the sample containing no particles. Examination of the
20 samples showed that the shape of the particles had not been changed significantly but their size had been reduced to about 50 - 70 μm .

Example 2

PVC pellets (EVC Compounds RG7-760-1476) were tumble blended with cross-linked acrylic particles as described in Example 1 and extruded into sheet at 180°C as described
5 in Example 1.

A sample without particles was made in the same way. The gloss was measured as described in Example 1 and the results are as shown in Table 2.

10

Table 2

Particle content (wt%)	Surface	Gloss units
0	hc	80
	lc	37
10	hc	54
	lc	20
20	hc	11
	lc	8.5

Example 3

Particles of a green coloured cross-linked acrylic polymer
15 were made from a monomer mixture comprising 84% MMA, 15.5% butyl acrylate and .0.5% ethylene glycol dimethacrylate together with stabilisers, initiators and a chain transfer agent as described in Example 1.

20 The particles were ground and sieved as before. An impact modified grade of acrylic moulding polymer (DIAKON™ ST35G8) was coloured using a green pigmented masterbatch at 8% wt. The green particles were compounded into the base polymer on the twin screw extruder and the resulting

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pellets were injection moulded using a Colourstubbe injection moulding apparatus at 230°C to form a 75 x 50 x 3 mm plaque sample. The gloss was measured as described earlier and the results are shown in Table 3.

5

Table 3

Particle content (wt%)	Gloss units
0	85
5	15
10	8
20	7

Example 4

- 10¹ Cross-linked acrylics polymer was prepared by bulk polymerisation of 83.18 wt% MMA, 14.68 wt% co-monomer (n-butyl acrylate) 0.61 wt% cross-linker, 0.49 wt% of chain transfer agent and 0.05 wt% initiator.
- 15 The polymer was ground and sieved to produce a particle size distribution wherein 36.7% w/w lay between 60 and 100 mesh (250 and 150 μm) and 35.1% w/w were between 150 and 30 μm and the material had a weight average particle diameter of 187.9 μm .
- 20 8 wt% of the particulate polymer was compounded into a commercially available impact modified acrylic copolymer (DIAKON™ ST35G8 as described above) using a ZSK30 co-rotating twin screw extruder at 230°C as described in
- 25 Example 1.

The material thus obtained was co-extruded using a single screw extruder as an approximately 100 μm layer onto rigid PVC to form panels of approximately 1mm total thickness. The panels were impact tested following ASTM D4226 and the surface gloss was evaluated using a 75° meter to ASTM D3679 as described above. The results were as follows:

	ASTM D4226 Mean Failure Height (inches) = 11.1
	Gloss (75° obs) = 51
10	Appearance of sheet = Matte surface

Example 5

The particulate polymer of Example 4 was compared to cross-linked bead particles having weight averaged diameters of 20, 40, 80 and 100 μm (referred to as Examples 5.1, 5.2, 5.3 and 5.4 respectively).

The particulate polymer and the cross-linked bead particles were compounded into an acrylic copolymer (as described in example 4) at a loading of 5 wt%, using a ZSK30 co-rotating twin screw extruder at a temperature of 230°C. Co-extruded sheet of nominal thickness approx. 1mm was produced with the acrylic material forming a cap of thickness approximately 100 μm . The surface gloss of the sheets was measured using a Rhopoint Novogloss Gloss Meter and the results obtained are shown in the table below.

Sample	Initial particle diameter/ μm	20° Gloss	60° Gloss	85°C
Eg 4	190	3.9+/-0.2	29.8+/-0.5	33.5+/-1.2
Eg 5.1	20	5.7+/-0.6	30.4+/-0.8	27.4+/-1.6
Eg 5.2	40	6.3+/-0.4	34.3+/-1.4	33.8+/-2.4
Eg 5.3	80	13.6+/-1	44.6+/-3.2	43.9+/-1.2
Eg 5.4	100	15.4+/-1.7	47.5+/-2.9	47.7+/-1

The gloss data for the cross-linked bead materials of Examples 5.1 to 5.4 exhibit a linear dependence of surface gloss on bead diameter for all gloss measurement angles. However, the material of Example 5 does not fit with these linear trends. In this case, individual particles could not be identified in the surface, while the presence of large discrete particle was observed for materials of Examples 5.3 and 5.4. More particularly, incident light optical microscopy confirmed that particles of the same size as added to the extruder were present in the material for Examples 5.

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Claims

1. A melt-processable thermoplastic composition comprising:

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c) 50-99.5 wt% of a melt-processable thermoplastic polymer; and

d) 0.5-50 wt% of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt% of methyl methacrylate (MMA), at least 0 - 50 wt% of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt% of a copolymerisable cross-linking monomer, said particles having a maximum dimension of 5 mm.

15

2. A composition according to Claim 1, wherein the melt-processable thermoplastic polymer forms a matrix and is of polymethylmethacrylate homopolymer or copolymer derived from a monomer mixture comprising 60 - 100 wt% methyl methacrylate and 0 - 40 wt% of at least one other copolymerisable alkyl acrylate or methacrylate.

3. A composition according to Claim 1 or Claim 2, wherein said particulate polymer is formed from the residues of a monomer mixture comprising at least 50 wt% methyl methacrylate.

4. A composition according to Claim 3, wherein said particulate polymer is formed from the residues of a monomer mixture comprising at least 1 wt% of a copolymerisable acrylic comonomer.

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5. A composition according to Claim 4, wherein said copolymer is an alkyl acrylate.
6. A composition according to any preceding claim,
5 wherein said monomer mixture includes at least 0.1 wt% of a comonomer which is capable of forming cross-linking with the polymer.
7. A composition according to any preceding claim,
10 wherein said particulate polymer is formed from the residues of a monomer mixture comprising 70 - 95 wt% MMA, 5 - 30 wt% of a copolymerisable acrylic comonomer and 0.1 - 5 wt% of a comonomer which is capable of forming cross-linking within the polymer.
- 15 8. A composition according to any preceding claim which includes at least 1 wt% and less than 40 wt% of said particulate polymer.
- 20 9. A composition according to any preceding claim, wherein the particles of said particulate polymer are of a size such that they could pass through a 500 μm sieve.
- 25 10. A composition according to any preceding claim, wherein at least 20 wt% of particles of said particulate polymer are between 60 (250 μm) and 80 (177 μm) mesh.
11. A method of preparing a melt-processable thermoplastic composition, the method comprising contacting:
- 30 a) 50-99.5 wt% of a melt-processable thermoplastic polymer; and

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- b) 0.5-50 %wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt% of methyl methacrylate (MMA), at least 0 - 50 wt% of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt% of a copolymerisable cross-linking monomer, said particles having a maximum dimension of 5 mm.
12. A method according to Claim 11, wherein said melt-processable polymer and said particulate polymer are not cast after contact together.
13. A method according to Claim 11 or Claim 12, wherein said melt-processable polymer and said particulate polymer are mixed by extrusion under conditions such that particles of said particulate polymer are broken down.
14. A method according to any of Claims 11 to 13, wherein said melt-processable polymer and said particulate polymer are not caused to chemically react during said mixing and/or extrusion.
15. A method of forming an article which comprises shaping a melt-processable thermoplastic composition according to any of Claims 1 to 10 or as prepared according to any of Claims 11 to 14 in order to form said article.
16. A method according to Claim 15, wherein said melt-processable thermoplastic composition is subjected to conditions such that particles of the particulate polymer in said melt-processable thermoplastic composition are broken down.

17. A method according to Claim 16, wherein said melt-processable thermoplastic composition is subjected to a shear rate of at least 100s^{-1} .
- 5 18. A method according to any of Claims 15 to 17, wherein said composition is extruded or co-extruded.
19. A method according to any of Claims 15 to 18, wherein said article includes a substrate and a capstock material
10 wherein said capstock material comprises said melt-processable thermoplastic composition.
20. A method according to any of Claims 15 to 19, wherein aid article is a building component.
- 15³ 21. A method according to any of Claims 15 to 20, wherein said article is a component for use in construction and is a co-extruded component comprising a substrate made of PVC, HIPS or ABS and said melt-processable thermoplastic
20 material provided as a capstock thereon.
22. A method according to any of Claims 15 to 21, wherein when a surface of the article formed of said thermoplastic composition is tested for impact resistance in accordance
25 with ASTM D4226, the mean failure height is not less than 7.5 inches (19.05 cm).
23. An article formed from a thermoplastic composition which comprises a melt-processable thermoplastic polymer
30 and a particulate polymer, wherein the weight averaged diameter of particles of said particulate polymer prior to formation of said article is greater than the diameter after formation of said article.

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24. A method of forming an article which comprises a capstock layer, the method comprising: selecting a melt-processable thermoplastic composition comprising a melt-
5 processable thermoplastic polymer and a particulate polymer wherein some of the particles of the particulate polymer have a diameter of $x \mu\text{m}$; and extruding, preferably co-extruding, said selected composition to form a capstock layer of a thickness less than $x \mu\text{m}$.

10

25. An article which includes a substrate and a capstock material prepared from a thermoplastic composition as described in any of Claims 1 to 10 or when prepared in a
15 method according to any of Claims 11 to 22 or 24.

15

26. An article according to any of Claims 19, 21, 24 or 25, wherein said capstock layer or material has a thickness of less than $200 \mu\text{m}$.

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(54) Title: MELT-PROCESSABLE THERMOPLASTIC COMPOSITIONS

(57) Abstract: A melt-processable thermoplastic composition is described, which comprises a) 50 - 99.5 wt.% of a melt-processable thermoplastic polymer and b) 0.5 - 50 wt.% of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt.% of MMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt.% of a copolymerisable cross-linking monomer said particles having a maximum dimension of 5 mm. The compositions have reduced surface gloss and may be useful for forming building components or in any other application in which a low gloss surface is required. A method of making the composition and its uses, for example its use as a capstock material, are also described.

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DECLARATION FOR UNITED STATES PATENT APPLICATION
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As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and that I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled MELT-PROCESSABLE THERMOPLASTIC COMPOSITIONS, the specification of which

☐ is attached hereto.

☐ was filed on _____, as Application Serial No. _____, and was amended on _____ [if applicable].

☒ was filed under the Patent Cooperation Treaty on August 16, 2000 Serial No. PCT/GB00/03184 the United States of America being designated, and was amended on _____ [if applicable].

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

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I HEREBY CLAIM foreign priority benefits under Title 35, United States Code §119(a)-(d) of §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number	Country	Foreign Filing Date	Priority Claimed
9919304.7	United Kingdom	August 17, 1999	YES

I HEREBY CLAIM the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

U.S. Provisional Application Number	Filing Date

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